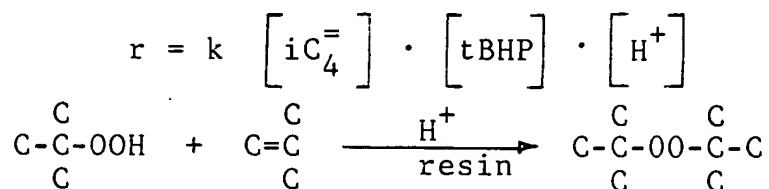


of the extracting ability of the large amount of isobutane. Especially low in concentration should be the t-butanol and hydroperoxide. Direct combustion of this stream as a composite with other streams containing more combustibles would be the anticipated mode of disposal.

Alkylation Of t-Butyl Hydroperoxide With Isobutylene

The alkylation of t-butyl hydroperoxide with isobutylene either pure or contained in a mixed butene stream is a very facile reaction which is acid catalyzed. Most of our work has been conducted with pure isobutene, with a limited amount of work done with normal butenes alone to establish that a nil amount of alkylation is occurring. Alkylation is effected by strong acid ion exchange resin of the sulfonic acid type preferably with the macro recticular structure that is most beneficial for organic reactions. Other solid acids are also effective and do not require the removal of the organics by distillation which is our preferred operating conditions. The reaction appears to be first order with respect to isobutylene, t-butyl hydroperoxide and acid.



Our alkylation is based on the following design case shown in Table 3.

Table 3
Alkylation Of t-Butyl Hydroperoxide
Design Case

Temperature	60°C
Pressure	200 psig
Catalyst	H ⁺ resin

tBHP:iC ₄ ⁼ : tBA (molar)	1.0:1.23:.49
WHSV	2.0 hr ⁻¹
Conversion M%	-
t-butyl hydroperoxide	100
isobutylene	81
Selectivity mol%	
di-t-butyl peroxide	100

t-Butyl hydroperoxide alkylation with isobutylene shows a reaction rate constant 10 to 20 times greater than the rate constant of alkylation of either water or methanol. As a consequence of this high rate constant, the avoidance of self alkylation to disiobutylene and more complete utilization of the contained isobutylene are possible in this system than in the alkylation of methanol. Ideal comparative systems for design or optimization consideration are the MtBE systems from isobutylene and tBA. The literature is replete with studies of various economic and technical optimizations. DtBP production has strong rate and equilibrium advantages.

Alkylation of tBHP has also been studied using mixed butene streams and tBA. Both are realistic potential candidates for the facile production of DtBP where the economics and markets exist for the production of gasoline octane enhancers of either the tBA alcohol type or the MtBE ether type. Our choice for this design is predicated on the basis of minimizing co-production. The alkylation block therefore functions as an internal process service and provides no economic upgrade although it does possess this capacity.

Played for economics only this section would be operated with a mixed butenes refinery stream to provide a dual upgrade of eventually acetone and/or tBA from the isobutene and an upgraded purified n-butene-1 stream for copolymerization with ethylene.

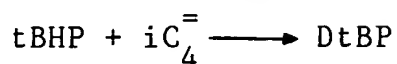
The design of Block 2 is based on the kinetics of the reaction which suggests that a plug flow reactor be used to attain the highest possible level of conversion of both the t-butyl hydroperoxide and isobutylene. We chose as the terminal point of the reaction a quantitative conversion of the t-butyl hydroperoxide and 81% conversion of the contained isobutylene. Much higher productivity is easily obtained from this section.

There are a number of approaches for the design of this alkylator. We have chosen a tube in shell configuration fabricated of 304 S.S. The tubes are filled with ion exchange resin and the reactants flow upward through the tubes while cooling water flows concurrently outside the tubes. This scheme provides maximum cooling during the earliest part of the reaction which evolves the most heat of reaction. DtBP is a more stable entity than tBHP to temperature and most every other catalyst including acids. For this reason we would prefer maximum reaction to occur at milder conditions than 60°C where the kinetics are favorable. The final portions of the reaction, we seek to push to completion, is then conducted at a somewhat higher temperature, where the reaction rate constant is greater, but the possibility of loss of active components is minimized.

Alternative approaches for this design are use of a packed bed reactor with multiple withdrawal and injection points to provide cooling and the use of a back mixed reactor cooled by normal means where a high percentage of the reaction is completed, followed by an adiabatic tubular plug flow reactor. In any of these systems the effluent should be monitored for strong acid and neutralized by weak salts if any is present. Data in Table 4 is used in the design of Block 2.

Table 4

Alkylation - Physical Properties

Heat Of Reaction

$$H = -22,100 \text{ BTU/mol/lb.}$$

Heats Of Vaporization

n-butene	C_4H_8	MW 56	11,400 BTU/mol/lb.
isobutylene	C_4H_8	MW 56	10,427 BTU/mol/lb.
t-butanol	$\text{C}_4\text{H}_{10}\text{O}$	MW 74	18,910 BTU/mol/lb.
acetone	$\text{C}_3\text{H}_6\text{O}$	MW 58	13,877 BTU/mol/lb.

Vapor Pressure

$$\text{Log}_{10} P = (-.2185 A/K) + B$$

$$K = ^\circ \text{ Kelvin}$$

$$P = \text{mm Hg}$$

	A	B
n-butene	622.6	7.882542
isobutylene	5742.9	7.601563
t-butanol	10413.2	9.193472
acetone	7641.5	7.904024

Heat Capacities

n-butene	.94 BTU/lb/ $^\circ\text{C}$
isobutylene	.939 BTU/lb/ $^\circ\text{C}$
t-butanol	1.31 BTU/lb/ $^\circ\text{C}$
acetone	.946 BTU/lb/ $^\circ\text{C}$

At this point in time we do not envision a need to purify the DtBP by distillation. This is possible if the need for it should be established. A particularly efficacious way is by azeotropic distillation with methanol.

Engineering Safety and Environmental

It is believed that t-butyl hydroperoxide is the highest peroxy homologue that possesses sufficient energy density (peroxy oxygen/weight) to detonate in the absence of oxygen. Di-t-butyl peroxide has a considerably lower energy density than does the hydroperoxide and accordingly is viewed as being quite a stable peroxide. The stability of any peroxide however should not be taken lightly because under proper conditions an adiabatic temperature rise can promote a very rapid decomposition to volatile products which can generate very high pressures with the potential to rupture reaction vessels. The safety concerns while less with DtBP must make provisions for the unexpected. The ability to quench when a certain threshold temperature is reached must be provided for in the design. A reservoir of tBA of suitable quantity to act both as a diluent source and as a dump would probably be the best means of controlling a runaway reaction. This reservoir could be common to both safety considerations in peroxidation and alkylation.

Environmental concerns arising from Block 2 are non-existent to the extent that no streams leave the confines of the plant and move into the environment for disposal.

Block 2 tBHP Alkylation

Process Description

T-butyl-hydroperoxide (tBHP) is alkylated with isobutylene to DtBP in the liquid phase in the presence of strong acid ion exchange resin. Low temperature (70°C) helps ensure resin stability while maintaining rates (30 min. res. time). Excess isobutylene (23%) ensures complete tBHP conversion in the plug flow reactor.

Excess isobutylene is removed in a single distillation step. Low base temperature of 115°C prevents DtBP decomposition. Product DtBP is immediately cooled and stored for feed to the Redox reactor.

Sizing-Influence of Redox Reaction

Size of Block 1 and 2 are dependent on DtBP utilization in the Redox reaction for the production of glycols.

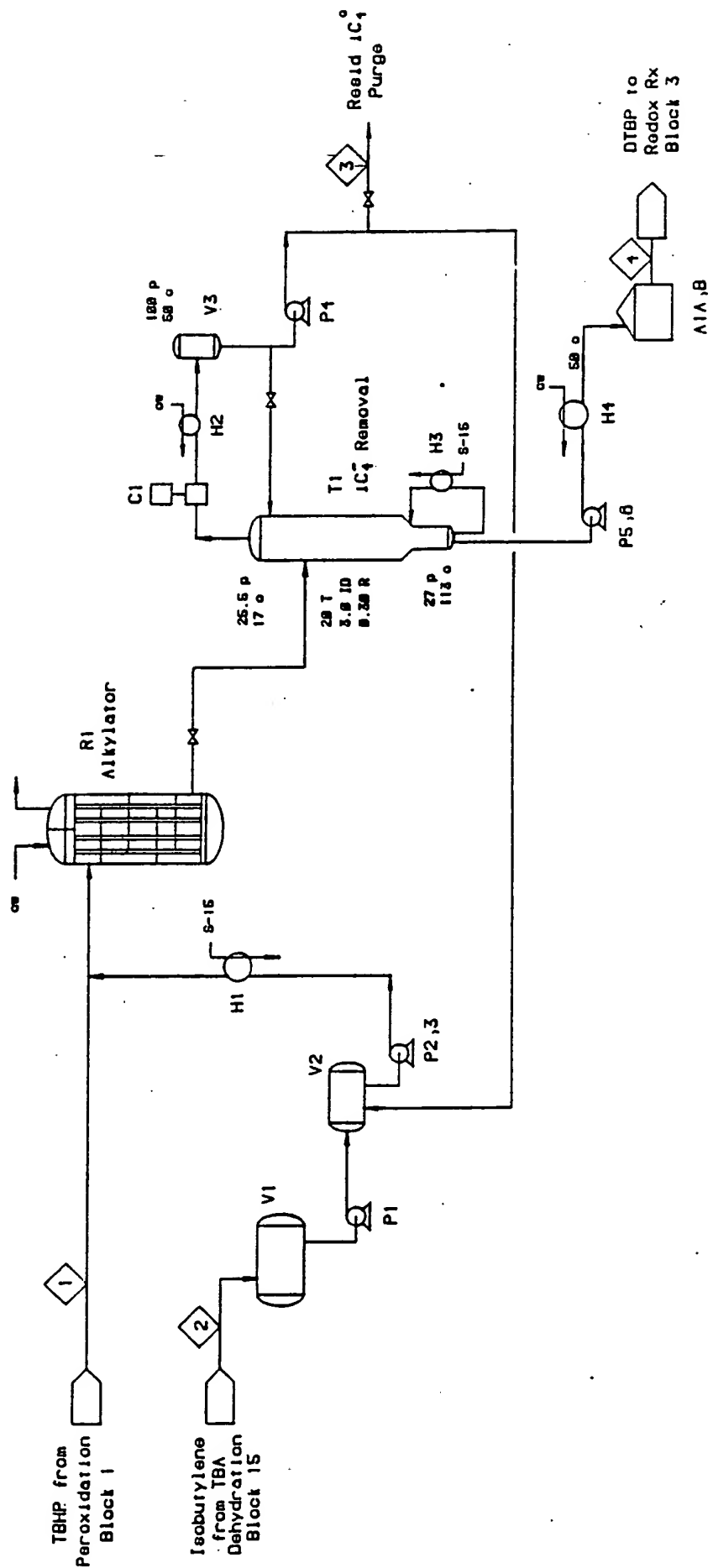
This case - tBHP utilization = 2.72 wt. ratio.

Range - tBHP utilization = 2.1 - 3.64 wt. ratio.

Utilities

	Units/lb. EG
Electricity KWH	.0015
Steam lb. S-15	.06
Cooling Water gal.	.8

FIGURE B-1
BLOCK 2 -- TBHP ALKYLATION
Detailed Process Flow Diagram



Block 2 Alkylation

Equipment Type	Delivered Equipment Cost M\$	BL/DEC Ratio	Battery Limits Cost M\$
Vessels	135.9	5.09	691.9
Atm. Tanks	157.2	2.55	400.9
Towers	39.2	5.89	230.9
Xchangers	699.5	1.91	1,336.0
Pumps	22.1	10.75	238.7
Compressors	<u>48.4</u>	<u>3.46</u>	<u>167.4</u>
Total	1,102.4	2.78	3,065.8

MATERIAL FLOWS

Alkylation - 200

	From 800	From 100	To 300	iC ₄ Purge
iC ₄ ⁼	280.17			
iC ₄		.25	.04	.21
nC ₄		.41	.19	.22
H ₂ O	19.35	21.55	40.90	
tBHP		280.16		
tBA	42.60	137.90	180.54	
DMK		8.55	8.55	.01
MeOH	29.17	8.54	37.71	
EtOH	33.86		33.86	
DtBP			280.16	

Alkylolation Block 200

		<u>Vessels</u>			
	gallons	Matrl.	Press. psia		
V0201	iC ₄ Feed	CS	150		
V0202	iC ₄ Surge	304 SS	175		
V0203	T1 OH Receiver	304 SS	130		
		<u>Towers</u>			
	Matrl.	Height x Dia.	Press.psig	Trays	
T0201	iC ₄ Removal	35' x 3'	130	20	304 SS
		<u>Atm. Tanks</u>			
	Gallons	Matrl.	Roof		
A020	1B DtBP Rundown	Al.	Fixed		
A020	1A DtBP Rundown	Al.	Fixed		
		<u>Heat Exchangers</u>			
	Area Sq.ft.	Type	Design	Matrl. SS/TS	Press psia SS/TS
H0201	iC ₄ Preheat	S&T	Std.	CS/304	50/200
H0202	T1 OH Cond.	S&T	Std.	304/304	130/50
H0203	T1 Reboil.	S&T	Thermo	CS/304	50/50
H0204	DtBP Cooler	S&T	Std.	304/304	50/50
R0201	Alkylator	S&T	Std.	304/304	200/50
				Design of F	250
					150
					250
					240
					160

Alkylation Block 200

<u>Pumps</u>						
	Units	HP	Type	Matrl.		
P0201	2	2.7	C	CS	P0204	Units HP Type Matrl.
P0202	2	4.8	C	316 SS	P0205	2 1.9 C 316 SS
P0203	1	4.8	C	316 SS	P0206	2 4.2 C 316 SS
						1 4.2 C 316 SS

<u>Compressor</u>			
	HP	Type	Matrl.
C0201 T10H Booster	83	Recip.	CS
			Driver
			Elect. Motor